(19) World Intellectual Property Organization International Bureau





(43) International Publication Date 31 January 2002 (31.01.2002)

PCT

(10) International Publication Number WO 02/07791 A2

(51) International Patent Classification7: A61L 15/00

(21) International Application Number: PCT/US01/21869

(22) International Filing Date: 11 July 2001 (11.07.2001)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data: 60/220,529

24 July 2000 (24.07.2000) US

- (71) Applicant: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Midland, MI 48674 (US).
- (72) Inventor: ACHILLE, Felix; 2861 North Tupelo Drive, Midland, MI 48642 (US).
- (74) Agent: CHRISTY, M., Robert; The Dow Chemical Company, Intellectual Property, P.O. Box 1967, Midland, MI 48641-1967 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

 without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



4

(54) Title: THERMOPLASTIC SUPERABSORBENT POLYMER BLEND COMPOSITIONS AND THEIR PREPARATION

(57) Abstract: An extrudable thermoplastic superabsorbent polymer blend composition is disclosed. The blend compositions are especially well suited for preparation of extruded or molded articles such as monolayer films, multilayer films, nonwoven webs, sheets, foams, profiles, multilayer laminates, fibers, tubes, rods or pipes which in turn are well suited for preparation of power and communication cables or disposable absorbent articles such as diapers, sanitary napkins, tampons, incontinence products, hospital gowns or bed pads.

THERMOPLASTIC SUPERABSORBENT POLYMER BLEND COMPOSITIONS AND THEIR PREPARATION

The present invention relates to a thermoplastic polymer blend composition comprising a superabsorbent polymer and method of preparation thereof.

5

10

15

20

25

30

Superabsorbent polymers are well-known materials that are used in a variety of applications ranging from personal care articles such as diapers to water barrier applications in the construction industry to water blocking agents in communications cables to liquid absorbers in food packaging systems. These polymers are known to absorb several times their weight of, for example, moisture, water, saline solution, urine, blood, and serous body fluids.

One of the challenges of using superabsorbent polymer particles within an absorbent device is the containment or fixation of the superabsorbent polymer particles. Depending on the particular absorbent device, different approaches to contain or fix the superabsorbent polymer particles have been taken. For example, disposable absorbent products such as diapers, sanitary napkins, tampons, and incontinence products, typically comprise a matt or batt wrapped with a liner wherein the batt usually comprises the superabsorbent polymer in particulate form, see U.S. Patent No. 3,670,731. However, loss of particles and/or redistribution of the particles within the device, sometimes referred to as shakeout, often occurs.

An attempt to reduce shakeout is taught in U.S. Patent No. 4,806,598 which discloses nonwoven webs made from a thermoplastic polymer composition comprising a polyoxyethylene superabsorbent comprising a soft segment bonded to a hard segment through a reaction with a third segment and a thermoplastic polymer. However, there is little interaction between the polyoxyethylene superabsorbent and the thermoplastic polymer and the blends are not stable with regard to phase separation. Further, webs made from the thermoplastic polymer composition do not demonstrate adequate wet strength and attempts to improve the wet strength of the webs by replacing some of the thermoplastic polymer composition with a low density polyethylene results in substantially decreasing the water absorbency of the web.

In power and communication cable applications different approaches have been tried to bind or fix superabsorbent polymers as water-blocking agents. For example, see U.S. Patent No. 4,966,809 which discloses water-blocking tapes made by mixing a

superabsorbent polymer and a polymeric binder and then spreading the mixture on nonwoven fabrics, see U.S. Patent No. 5,461,195 which discloses a superabsorbent polymer mixed with a thixotropic agent to form a gel which is used to fill the spaces between the wires of the cable or see U.S. Patent No. 5,925,461 which discloses strengthening members or buffer tubes coated or impregnated with a hot melt adhesive comprising a super absorbent.

5

10

15

20

25

30

Mixtures of superabsorbent polymers and binders are characterized by a number of disadvantages and/or limitations, such as manufacturing and operating temperature limitations, lack of adhesion to the substrates to which the mixture is applied, and delaminating when the article is pulled in the tensile direction, that contribute to abrasion when the article is being fabricated. Further, tapes add additional components in the construction of cables causing considerable unwanted increases in their costs and diameters. Cables using filler gels are characterized by a number of disadvantages and/or limitations such as manufacturing and operating temperature limitations, formation of voids which lead to paths of water migration, and difficulties meeting industry standards.

Other methods to bind superabsorbent polymers are known. For example see, U.S. Patent No. 5,516,585 which discloses a method of coating discontinuous fibers with a thermoset binder material which binds particles of superabsorbent wherein the discontinuous fibers are formed into a web. In a method described in U.S. Patent No. 4,392,908 superabsorbent polymer particles are coated with a thermoplastic resin and fixed to a water-absorbent substrate by applying heat to soften the thermoplastic coating of the particles and pressing the particles and substrate to cause the particles to bind to the substrate. These methods are expensive requiring specialized equipment and/or many steps and have limited commercial applicability.

Further, films and laminates of superabsorbent polymers have been made from solutions of superabsorbent polymers followed by heating and/or removing the solvent. For examples of cross-linked superabsorbent polymer films and laminates see U.S. Patent Nos. 3,926,891, 4,076,673 and 4,117,184. For examples of non-cross-linked superabsorbent polymer films see U.S. Patent Nos. 3,935,099, 3,997,484 and 4,090,013. U.S. Patent No. 3,669,103 describes a method to make thin foamed polyurethane thermoset sheet comprising superabsorbent polymer particles. Unfortunately, these methods of forming films, laminates and sheet are impractical for large-scale commercial use.

It would be desirable to have a superabsorbent polymer composition with improved containment of superabsorbent polymer particles for use in absorbent devices such as personal-care articles and cable wrap components while maintaining good absorptive properties. Further, it would be desirable for such a superabsorbent polymer composition to be easily and conveniently shaped into a variety of useful forms, especially on a commercial scale.

The present invention is such a composition. It is a thermoplastic superabsorbent polymer blend composition comprising (a) a superabsorbent polymer (b) a thermoplastic resin and optionally (c) a surfactant wherein components (a) and (b) interact with each other ionically or covalently and the blend composition can be formed by extrusion, for example, into film, sheet, laminates, foams, profiles and injection molded articles.

In another aspect, the present invention is a process for preparing the abovementioned extrudable thermoplastic superabsorbent polymer blend composition.

10

15

20

25

30

In a further aspect, the present invention involves a method of extruding or molding the abovementioned extrudable thermoplastic superabsorbent polymer blend composition.

In yet a further aspect, the invention involves extruded (for example, film, sheet, foam, and laminates) or molded articles of the abovementioned extrudable thermoplastic superabsorbent polymer blend composition.

In yet a further aspect, the invention involves articles comprising extruded or molded articles of the abovementioned extrudable thermoplastic superabsorbent polymer blend composition.

The blend compositions and extruded and molded articles of the present invention may be employed in a wide variety of uses as are known in the art, such as, for example, the assembly or construction of cable wrap components and various disposable absorbent articles, such as sanitary napkins, disposable diapers, hospital gowns, and bed pads

The superabsorbent water-swellable or lightly cross-linked hydrophilic polymers suitably employable in the present invention can be any of the known hydrophilic polymers that are capable of absorbing large quantities of fluids. These polymers are well known in the art and are widely commercially available.

Examples of some suitable polymers and processes, including gel polymerization processes, for preparing superabsorbent polymers are disclosed in U.S. Patent Nos. 3,997,484; 3,926,891; 3,935,099; 4,090,013; 4,093,776; 4,340,706; 4,446,261; 4,683,274; 4,459,396; 4,708,997; 4,076,663; 4,190,562; 4,286,082; 4,857,610; 4,985,518; and

5,145,906. In addition, see Buchholz, F.L. and Graham, A.T., "Modern Superabsorbent Polymer Technology," John Wiley & Sons (1998) and Lisa Brannon-Peppas and Ronald S. Harland, "Absorbent Polymer Technology" Elsevier (1990).

Preferred superabsorbent polymers are prepared from water-soluble α,β-ethylenically unsaturated monomers such as monocarboxylic acids, vinyl polycarboxylic acids, acrylamide and their derivatives. More preferred superabsorbent polymers are cellulosic or starch-graft copolymers, such as starch-g-poly(acrylonitrile), and starch-g-poly(acrylic acid); polyacrylamides; polyvinyl alcohols; poly(acrylic acids); high molecular weight polymers, preferably cross-linked, of ethyleneoxide (EO) and propyleneoxide (PO); copolymers of sulfonic acid group containing monomers, such as vinyl sulfonic acid, sodium sulfoethyl methacrylate, 2-Acrylamido-2-Methylpropane-sulfonic acid or the sodium salt (AMPS).

5

10

15

20

25

30

Most preferred superabsorbent polymers are crosslinked, partially neutralized and/or surface treated. Preferably, the level of crosslinking is selected to give the desired swelling characteristics for the particular application. Generally, the degree of neutralization is from 30 to 100 percent, more preferably from 50 to 80 percent. Neutralization with a basic substance containing a Group I metal ion, such as sodium, is preferred. A preferred surface treatment consists of a post polymerization reaction to effect the surface crosslinking of the superabsorbent polymer.

The amount of the superabsorbent polymer to be included in the thermoplastic superabsorbent polymer blend composition according to the present invention will vary depending, for example, upon the type of superabsorbent polymer used, the type of thermoplastic resin used, the desired extruded or molded product, the extruded or molded product's end use application, the desired level of blocking, absorbing or stopping the migration of water and/or other fluids in the end use application.

The superabsorbent polymer is present in an amount equal to or greater than about 1 part per weight, preferably equal to or greater than 5 parts per weight, more preferably equal to or greater than 10 parts per weight, even more preferably equal to or greater than 15 parts per weight and most preferably equal to or greater than 20 parts per weight based on the weight of the thermoplastic superabsorbent polymer blend composition. The amount of superabsorbent polymer is present in an amount equal to or less than 70 part per weight, preferably equal to or less than 65 parts per weight, more preferably equal to or less than 60 parts per weight, even more preferably equal to or less than 55 parts per weight and most

preferably equal to or less than 50 parts per weight based on the weight of the thermoplastic superabsorbent polymer blend composition.

In addition to a superabsorbent polymer, the blend composition of the present invention contains at least one thermoplastic resin that interacts (that is, ionically, covalently) with the superabsorbent polymer. For example, a thermoplastic resin having an acyl groups which can undergo nucleophilic attack resulting in a substitution reaction in which a leaving group, such as -OH, -Cl, -OOCR, -NH2 or -OR, is replaced by another basic group present in the superabsorbent polymer. Another example is a thermoplastic resin containing carbonyl groups that can undergo a nucleophilic attack gaining a proton and adding another basic group present in the superabsorbent polymer. Under these conditions the reaction product of the thermoplastic resin and superabsorbent polymer may form a uniform and/or co-continuous non-separating polymer blend.

10

15

20

25

Preferred thermoplastic resins have functional groups such as acyl or carbonyl groups (for example, α,β -unsaturated carbonyl compounds, hydroxy acids, dicarboxylic acids, keto acids, anhydrides, carboxylic acids, aldehydes, ketones, acid halides, esters, amides, etc.), sulfonyls, sulfonyls halides, ethers, phenols, aryl halides, epoxides, carbohydrates, alcohols, azides, and amines.

The preferred thermoplastic resins are acrylic polymers, with polyacrylic acid (PAA), ethylene and acrylic acid copolymers (EAA), ethylene, t-butylacrylate and acrylic acid terpolymer (EtBAAA), ethylene and methacrylic acid copolymers (EMAA), ionomers of ethylene and methacrylic acid copolymers especially the sodium and zinc ionomers, ethylene, vinyl acetate and carbon monoxide terpolymers (EVACO), ethylene and carbon monoxide copolymers (ECO), ethylene, acrylic acid and carbon monoxide terpolymers (EAACO), ethylene, n-butylacrylate and carbon monoxide terpolymers (EnBACO) and blends thereof being most preferred.

The most preferred thermoplastic resins are 1) an EAA copolymer, wherein the EAA copolymer may be a blend of two or more EAA copolymers, preferably having a composition from 10 to 20 weight percent acrylic acid based on the weight of the copolymer and a melt flow rate (MFR) from 100 to 200 grams per 10 minutes (g/10 min.) under conditions of 190°C and an applied load of 2.16 kg., 2) ionomers of EMAA, preferably the zinc ionomer, 3) EVACO, preferably having a carbon monoxide content of at least 9 percent based on the weight of the terpolymer or 4) blends thereof.

The thermoplastic resin is present in an amount equal to or greater than 30 part per weight, preferably equal to or greater than 35 parts per weight, more preferably equal to or greater than 40 parts per weight, even more preferably equal to or greater than 45 parts per weight and most preferably equal to or greater than 50 parts per weight based on the weight of the thermoplastic superabsorbent polymer blend composition. The amount of thermoplastic resin is present in an amount equal to or less than 99 parts per weight, preferably equal to or less than 95 parts per weight, more preferably equal to or less than 90 parts per weight, even more preferably equal to or less than 85 parts per weight and most preferably equal to or less than 80 parts per weight based on the weight of the thermoplastic superabsorbent polymer blend composition.

It should be apparent to those having ordinary skill in the art that the present invention contemplates blends containing two or more superabsorbent polymers and/or blends of two or more thermoplastic resins (for example, EAA/EVACO, EMAA/EAA, a first EAA/a second EAA).

10

15

20

25

30

While the blend compositions of the present invention contain at least one superabsorbent polymer, such blend compositions may or may not be superabsorbent, depending upon the level and absorbency of the superabsorbent polymer in the blend composition and the availability of the superabsorbent polymer to aqueous media.

The blend compositions of the present invention can be further blended with other thermoplastic polymers, preferably low density polyethylene (LDPE), linear low density polyethylene (LLDPE), very low density polyethylene (VLDPE), polypropylene (PP), polystyrene (PS), ethylene and methylacrylate copolymer (EMA), ethylene and ethylacrylate copolymer (EEA), ethylene and n-butylacrylate copolymer (EnBA), polyethylene grafted with maleic anhydride grafted (PE g-MAH), ethylene and vinyl acetate copolymer (EVA), ethylene and vinyl acetate copolymer grafted with maleic anhydride grafted (EVA g-MAH), or combinations thereof.

The blend compositions of the present invention may further comprise additional additives commonly used in compositions of this type such as lubricants, extenders, compatibilizers, plasticizers, low and high molecular weight waxes, surfactants, stabilizers, pigments, carbon black and fillers such as talc, titanium dioxide (TiO₂), calcium carbonate (CaCO₃), magnesium oxide (MgO), and mica.

The blend compositions of the present invention may further be blended with a solvent to form a dispersion or paste. One skilled in the art can readily choose the type and amount of solvent depending on the particular end use.

5

10

15

20

25

30

As used herein, the phrase "extrudable thermoplastic superabsorbent polymer blend composition" means that: (1) the blend composition is melt processable in an extrusion, injection molding and/or blow molding process, (2) the extrudate is either commuted to pellets or directly extruded or molded by extrusion fabrication technique, (3) the pellets have a measurable melt flow rate, melt draw rate and melt strength sometimes referred to as melt tension and (4) the pellets can be re-extruded by an extrusion fabrication techniques. Preferably, the blend compositions of the present invention do not cause plugging, die-face build up, surging, melt fracture, pinholes, tearing and/or poor extrudate properties (that is, strand dropping, delamination) during the extrusion process.

A melt indexer is used to determine melt flow rate (MFR), melt tension and draw down rate. MFR is determined by ASTM D 1238; the run conditions (that is, temperature and applied load) depend upon the thermoplastic resin used. Melt tension is determined from a load cell attached at the bottom of the melt indexer which measures the load required to pull the extrudate from the die of the melt indexer to a take up reel at some given speed measured in feet per minute (fpm). The draw down rate (fpm) is determined by how fast the extrudate coming out of the melt indexer can be pulled before it breaks. When MFR conditions are selected to give a MFR between 0.1 and 300 g/10 min. the thermoplastic superabsorbent polymer blend composition has a melt draw down rate between 5 and 100 fpm and a melt tension between 0.1 and 10.

The components of the extruded blend composition can be co-continuous or separate phases (one being continuous and one or more being dispersed therein) as long as phase separation does not have a significant deleterious effect on the melt processability or performance of the blend composition.

Preferred extrusion fabrication techniques include preparing melt blown or cast films; extrusion coating; (co)extruding nonwoven webs, including spun bond nonwoven webs, melt blown nonwoven webs, or composites comprising combinations thereof, sheets, foams, profiles, multilayer laminates, fibers including monofilament fibers and bicomponent monofilament fibers, tubes, rods or pipes; blow molding articles; injection molding articles (including solid, co-injection, structural foam and gas assist injection molding). Preferred nonwoven webs comprise spun bond nonwoven webs comprising one.

or more bicomponent fiber, melt blown nonwoven webs comprising one or more bicomponent fiber, and a composite structure comprising at least one layer of one or more spun bond nonwoven web and at least one layer of one or more melt blown nonwoven web wherein one or more layers of the composite comprise bicomponent fibers.

5

10

15

20

25

30

The thermoplastic superabsorbent polymer blend compositions of the present invention can be extruded into foam using a chemical or physical blowing agent. Further, the thermoplastic superabsorbent polymer can be blended with other miscible or compatible thermoplastic polymers such as LDPE, LLDPE, VLDPE, PP, PS, EEA, EMA, ENBA, PE g-MAH, EVA, or EVA g-MAH. One skilled in the art can choose the type and amount of blowing agent as well as other polymers to blend with the thermoplastic superabsorbent polymer for the particular end use in order to modify the cell size, structure, porosity, microcellular nature and absorbency characteristics of the thermoplastic superabsorbent polymer foam as desired.

The blend compositions to make foam may further comprise additional additives commonly used in compositions of this type such as lubricants, extenders, nucleators, compatibilizers, plasticizers, low and high molecular weight waxes, surfactants, stabilizers, pigments, carbon black and fillers such as talc, TiO₂, CaCO₃, MgO, and mica.

Further, extruded pellets or sheet can be compression molded; calendered; vacuum formed or thermoformed. Preparation of the thermoplastic superabsorbent polymer blend compositions of this invention can be accomplished by any suitable mixing means known in the art. Typically the components and any additional additives are blended in a tumbler or shaker in powder, particulate and/or pellet form with sufficient agitation to obtain thorough distribution thereof. The dry-blended formulation can further be subjected to shearing stresses at a temperature sufficient to heat soften and melt-mix the polymers, for example in an extruder, with or without a vacuum, or other mixing apparatuses (for example, a Banbury mixer, roller mill, Henschel mixer, a ribbon blender). Further, additional powder, particulate and/or liquid additives may be added to the composition during the mixing process. Such melt-mixed material can be extruded to make the finished article (that is, film, sheet, foam, profile) or recovered in the form of a pellet, powder or flake, preferably a pellet. The extrudate may be commuted to pellets by any conventional means such as a strand chopper or an underwater die face cutter.

The extrudate from the melt-mixing may be cooled by any method known in the art, such as air cooled, gas cooled, belt cooled, and liquid cooled by passing through a liquid

bath. Preferably a stainless steel belt cooler, for example manufactured by Sandvik Process Systems, Sweden or a Compact Conti Cooler manufactured by BBA AG, Switzerland, or an aqueous liquid bath, preferably where the pH is less than 1.0 or an aqueous liquid bath with a water hardness of greater than 25 French Degrees, more preferably an aqueous liquid bath with a specific gravity greater than 1.05 as measured with a desitometer is used. The aqueous bath preferably contains a saturated salt solution containing a Group 1 metal ion, preferably sodium, such as sodium chloride (NaCl), sodium sulfate (Na₂SO₄), and sodium bicarbonate (NaHCO₃).

Further, to minimize the effect of the water on the superabsorbent compound it has been discovered that maintaining the temperature of the liquid bath less than 23°C and preferably less than 20°C effectively cools the pellets without grossly activating the superabsorbent polymer in the blend composition.

10

15

20

25

30

It has further been found that when using an underwater pelletizer, optimizing the transfer pipe length from the underwater pelletizer to the separating dryer minimizes the activation of the superabsorbent polymer in the blend composition.

Blowing cool air in the pellet-collecting vessel, such as the use of a fluidized bed cooler, to drive away the remaining moisture on the pellets further improves the drying process.

It has been found using a process comprising an underwater die face cutter, a saturated NaHCO₃ solution having a specific gravity greater than 1.05 and a temperature less than 20°C and blowing cool air in the pellet-collecting vessel yields an extrudable thermoplastic superabsorbent polymer blend composition in a free flowing plastic pellet form having a moisture content ranging from 0.2 to 4 weight percent depending on the superabsorbent polymer, concentration of superabsorbent polymer in the blend composition and the base thermoplastic resin, wherein moisture weight percent is based on the weight of the blend composition.

The melt-mixed material (powder, flake or pellet) can be re-extruded or molded to make the finished article. Dry blends of the blend compositions can also be directly injection molded or metered into another melt fabrication process without pre-melt-mixing.

The extrudable thermoplastic superabsorbent polymer blend compositions of the present invention are useful in the pellet, flake or powder form for use in cat litter, solidified gases/fluids, gelled ice, soil conditioner, frost control, agricultural delivery systems, gelled biohazards, spill control, for the fabrication of articles such as foams, such as closed, semi-

porous or microcellular or open cell, bicomponent fibers and waterproof or waterblocking coating systems, thick film or sheet for such applications as disposable absorbent articles, such as sanitary napkins, disposable diapers, hospital gowns, and bed pads, films for such applications as moisture sensitive systems, moisture, such as water, absorbing structures, for example in packaging, transportation, and construction applications, diaper backing, meat trays, carpet backing or power and communication cable water-blocking tapes, film for laminate structures such as laminated foam structures, laminated non-woven structures, film for laminates for such applications as cable shielding tapes for use in power cables or communication cables, such as fiber optical cables, copper pair cables, and coaxial cables as disclosed in U.S. Patent Nos. 3,795,540, 4,449,014, 4,731,504 and 4,322,574.

It is further desirable that when the present invention is used in the construction of cables for example, power cables and communication cables, such as fiber optical cables, copper pair cables, coaxial cables, the cables meet certain requirements of water penetration. Most desirably, a cable structure comprising an extrudable thermoplastic superabsorbent polymer blend composition resists penetration, sometimes referred to as water blocking, of water through the cable in the longitudinal direction.

To illustrate the practice of this invention, examples are set forth below. Examples

Thermoplastic Superabsorbent Polymer Blend Compositions

5

10

15

20

25

30

In Comparative Examples A to ZZ and Examples 1 to 13 different thermoplastic resins are melt blended in a Brabender Plasticoder with CABLOCTM 850-13 a sodium polyacrylate superabsorbent polymer that is surface cross-linked having a particle size distribution of 1 to 300 micrometers available as a powder from Stockhausen and supplied by the Stewart Superabsorbents LLC. Unless otherwise noted, the ratio of superabsorbent polymer to thermoplastic resin is 40:60. The Brabender Plasticoder conditions are: Barrel temperature ranging from 275 to 420°F depending on the thermoplastic resin being used; Mixing revolutions per minute (RPM) are 80; and Mixing times range from 1.5 to 2 minutes. A melt indexer is used to determine the melt flow rate, melt tension and melt draw down rate of the polymer blends

Table 1 lists the compositions for Comparative Examples A to ZZ and Examples 1 to 13 and their properties. In Table 1 blend compositions which can be melt blended in some fashion and pressed into a shape or molded into a sheet or an article, but do not meet the criteria set forth herein as extrudable are designated not extrudable.

Comparative Examples AB to AN and Examples 14 to 17 are compounded on a WP ZK30 twin screw extruder. The SAP and the polymer are fed separately into the feed section of the extruder, the vent port of the extruder is open to the atmosphere and the extrudate is air-cooled.

The compositions of Comparative Examples AB to AN and Examples 14 to 17 and extruder temperatures are given in Table 2, the superabsorbent polymer is present in parts by weight based on the weight of the thermoplastic superabsorbent polymer blend composition. In Table 2 compositions that demonstrate die face build-up and/or plugging are designated "not" extrudable.

5

Table 1

sition	Extrudable	S.	o _N	8	Š	9	S S	No No	SO.	No.	No	No	No	No	No	No	So	No	No	No	No	S S	No	oN		No No
er Blend Compo	Draw Rate, fpm			₽																						
bsorbent Polyme	Melt Tension, units			9.0																						
Thermoplastic Superabsorbent Polymer Blend Composition	MFR, g/10 min	5.20	1.98	4.5	0.72	1.33	11.2	0.417	1.16	0.594	3.26	7.6	5.8	0.42	1.30	0.44	0.28	0.5	0.1	0.1	0.1		1.43	2.62		2.41
Ė	MFR, Condition	ш	ш	ш	ш	ш	В	ш	ш	ш	ш	_	g	ш	ш	ш	ш	ш	ш	ш	ш	ш	ш	160 °C /	0.353 Kg	ш
esin	Туре	HOPE	LDPE	LDPE	LDPE	LLDPE	LLDPE	VLDPE	VLDPE	INSITE IN PE	INSITE PE	ЬР	PS	EMA	EMA	EnBA	PE g-MAH/high MAH	EVA g-MAH/high MAH	EVA g-MAH/high MAH	LLDPE g-MAH/high MAH	EPDM g-MAH/medium MAH	PE g-MAH MAH	EA terpolymer g-MAH/high MAH	PP g-MAH/very high MAH		Anhydride Modified EVA
Thermoplastic Resin	Supplier	Equistar	Dow Chemical Co.	Dow Chemical Co.	Dow Chemical Co.	Dow Chemical Co.	DuPont Dow	Montell	Dow Chemical Co.	Chevron	Chevron	Chevron	Dow Chemical Co.	DuPont	DuPont	DuPont	DuPont	DuPont	DuPont	DuPont		DuPont				
	Grade	ALATHON' M6060	LDPE 4005	LDPE 4012	LDPE 681	DOWLEX™ 2247A	ASPUN ^{IM} 6821	ATTANE™ 4201	ATTANE 4402	AFINITY ^{IM} 1880	ENGAGE™ 8200	PP 861	PS 680	Chevron 2252-T	Chevron 2255	Chevron 1802	ENGAGE SM8400	FUSABOND TM 190D	FUSABOND 197D	FUSABOND 226D	FUSABOND 274D	FUSABOND 413D	FUSABOND 423G	FUSABOND 353D		BYNEL ^{IM} E418
Example Com. Ex.		A	8	O	۵	ш	L	ŋ	I		-	¥	J	Σ	z	0	Ь	a	<u>د</u>	S	۰	ے ا	>	*		×
Example																										

	sition	Extrudable	2	ş	ટ	2	S S	<u>8</u>	8	2	S _O	2	N _O	S S	ON	<u>8</u>	ON	N _O	No	ON	No No	S _O	No No	S	ON	2	οN	ХөХ	Yes
	er Biend Compo	Draw Rate, fpm																										2	20
	absorbent Polyn	Melt Tension, units																										1.5	0.5
	Thermoplastic Superabsorbent Polymer Biend Composition	MFR, g/10 min	1.71	0.84	0:00	0.75	1.24	2.77	5.42	11.58	9.72	3.82	0.25	18.2	3.62	4.6	3.1	4.75	5.6	13.68	1.5	4.4	2.3		24.52	7.5	0.33	3.1	7.28
		MFR, Condition	Ш	ш	ш	ш	ш	ш	ŋ	5	5	g	g	5	5		9	g	O	m	a	ပ	ပ	ပ	ပ	ш	ш	ш	ш
Table 1 Continued	esin	Туре	Acid/Acrylate Modified EVA	Anhydride Modified LLDPE	Anhydride Modified PP	Anhydride Modified EA	Anhydride Modified EVA	Anhydride Modified HDPE	SBS block copolymer	SIS block copolymer	SBS block copolymer	SEBS block copolymer	SEBS block copolymer	SIS block copolymer	SBS block copolymer	SBS block copolymer	SBS block copolymer	Ethylene-Styrene Interpolymer	Ethylene-Styrene Interpolymer	EVA, 28% VA	EVA, 49% VA	CoPolyester hot meit adhesive	EMS Am. Grilon, Inc CoPolyester hot melt adhesive	Polyamide Resin	Polyamide Resin	Thermoplastic Phenoxy Resin	ECO, 1% CO	EnBACO	EVACO
	Thermoplastic Resin	Supplier	DuPont	DuPont	DuPont	DuPont	Equistar	Equistar	Firestone	Dexco Polymers	Dexco Polymers	Sheli	Shell	Dexco Polymers	Phillips	Phillips	Dexco Polymers	Dow Chemical Co.	Dow Chemical Co.	DuPont	DuPont	EMS Am. Grilon, Inc	EMS Am. Grilon, Inc	Henkel	Henkei	Dow Chemical Co.	Dow Chemical Co.	DuPont	DuPont
		Grade	CXA 3101	CXA 4105	BYNEL 50E561	BYNEL 2174	PLEXAR ^{1M} 3	PLEXAR 206	STEREON TM 841A	VECTOR ¹⁴⁴ 4211	VECTOR 4461	KRATON ¹⁴ G1657	KRATON FG1901X	VECTOR 4411	Phillips DK-11	Phillips K-10	VECTOR 8508	ESI DE 200	ESI DS 201	ELVAX ^{IM} 3180	ELVAX VOW	GRILTEX ^{IM} 9	GRILTEX D 1519EGF	MACROMELT ^{IM} 6238	MACROMELT 6206	PHAE	LDPE 457	ELVALOY ^{IM} HP441	ELVALOY EP4924
	Com. Ex.		,	Z	ΑA	BB	8	QQ	EE	표	99	壬	=	3	XX	3	MM	Z	8	Ь	g	RR	SS	۴	3	8	MM		
	Example																											-	2

Table 1 Continued

		_	,		_	_		_				_	_		
ition	Extrudable	Yes	N N	Yes	Yes	Yes	Yes	No.	Yes	Yes	Yes	Yes	Yes	Yes	S S
Blend Compos	Draw Rate, form	5			5	20	10		10	5	5	2	45	50	
bsorbent Polymer	Meit Tension, units	1.0			1.0	9.0	1.5		1.4	0.2	0.5	2.0	6.0	0.5	
Thermoplastic Superabsorbent Polymer Blend Composition	MFR, g/10 min	2.8	2.2	0.72	2.43	8.98	0.84	0.3	1.16	8.72	4.6	1.46	6.0	4.13	2.58
The	MFR, Condition	ш	ш	ш	ü	ш	В	В	62	ш	В	125 °C / 5.0 Kg	ш	ш	ш
esin	Туре	EEA	EAA, 6.5% AA	EAA, 9.7% AA	EAA;; 9.7% AA	EAA, 9.7% AA	EAA, 20.5% AA	EAA, 20.5% AA	EAA, 15.1% AA	EMAAA	EMAA	Na-EMAA lonomer	Zn-EMAA lonomer	Zn-EMAA lonomer	Zn-EMAA lonomer
Thermoplastic Resin	Supplier	Chevron	Dow Chemical Co.	Dow Chemical Co.	Dow Chemical Co.	Dow Chemical Co.	Dow Chemical Co.	Dow Chemical Co.	Dow Chemical Co.	Exxon	DuPont	DuPont	DuPont	DuPont	DuPont
	Grade	A702	PRIMACOR ^{IM} 3330	PRIMACOR 1410	PRIMACOR 1430	PRIMACOR 3460	XUS70751.17	PRIMACOR 5980	PRIMACOR blend (a)	ESCOR ¹¹⁴ ATX 325	NUCREL [™] 699	SURLYN ^{IM} 8660	SURLYN 1702	SURLYN 1702 (b)	SURLYN 1702 (c)
Example Com. Ex.			×					҂							77
Example		င		4	2	9	7		8	6	10	11	12	13	

EnBACO = ethylene, n-butylacrylate and carbon monoxide terpolymer EVACO = ethylene, vinyl acetate and carbon monoxide terpolymer EEA = ethylene and ethyl acrylate copolymer EAA = ethylene and acrylic acid copolymer AA = acrylic acid EMAA = ethylene and methacrylic acid copolymer EMAAA = ethylene and methyl acrylate and acrylic acid copolymer Condition B = 125°C/2.16 kg Condition C = 150°C/2.16 kg Condition E = 190°C/2.16 kg Condition G = 200°C/5.0 kg Condition L = 230°C/2.16 kg Na = sodium Zn = zinca 50/50 blend of PRIMACOR 3460 and PRIMACOR 5980 a 50/50 blend of SURLYN 1702 and CABLOC 850-13 a 40/60 blend of SURLYN 1702 and CABLOC 850-13

SIS = styrene, isoprene and styrene block copolymer SEBS = styrene, ethylene, butylene and styrene block terpolymer ESI = ethylene and styrene interpolymer block copolymer ECO = ethylene and carbon monoxide copolymer

SBS = styrene, butadiene and styrene block copolymer

EPDM = ethylene propylene diene monomer EA = ethylene and acrylate copolymer g-MAH = grafted with maleic anhydride EVA = ethylene and vinyl acetate copolymer

PS = polystyrene EMA = ethylene and methylacrylate copolymer EnBA = ethylene and n-butylacrylate copolymer

PE = polyethylene

PP = polypropylene

(a) a 50/50 biend of PRIMACOR 32 (b) a 50/50 biend of SURLYN 1702 (c) a 40/60 biend of SURLYN 1702 LDPE = low density polyethylene LLDPE = linear low density polyethylene VLDPE = very low density polyethylene

Table 2

Example	Example Com. Ex.		Thermoplastic Resin		Superabsorbent Polymer	Blend Composition, parts	sition, parts	Extruder Temperatures	Extrudable
		Grade	Supplier	Туре		Resin	SAP	냥	
	AB	LDPE 681	Dow Chemical Co.	LDPE	SAP-1	08	20	310-330	No
	AC	LDPE 681	Dow Chemical Co.	LDPE	SAP-1	75	52	310-330	S
	ΑD	LDPE 681	Dow Chemical Co.	LDPE	SAP-1	65	38	310-330	8
	AE	LDPE 681	Dow Chemical Co.	Трре	SAP-1	09	40	310-330	No
	AF	ATTANE 4201	Dow Chemical Co.	VLDPE	SAP-2	80	50	335-370	N _O
	AG	ATTANE 4203	Dow Chemical Co.	VLDPE	SAP-1	73	27	321-350	S S
	AH	ALATHON 6030 HPPE	Equistar	HDPE	SAP-2	80	20	335-370	S
	ΙĄ	DOWLEX 2045	Dow Chemical Co.	LLDPE	SAP-2	75	52	400-420	<u>8</u>
	₹	ELVAX 3180	DuPont	EVA, 28% VA	SAP-1	09	40	250-260	8
	AK	Aqua Calk (a)	Sumtomo Seika Chemical Co., Ltd.	Polyethylene Oxide(a)	SAP-1	09	40	250-260	No
	AL.	PRIMACOR 3330	Dow Chemical Co.	EAA, 6.5% AA	SAP-1	09	40	310-330	No No
14		PRIMACOR 3460	Dow Chemical Co.	EAA, 9.7% AA	SAP-1	09	40	250-260	Yes
	AM	PRIMACOR 5980	Dow Chemical Co.	EAA, 20.5% AA	SAP-1	09	40	250-260	No
15		PRIMACOR blend (b)	Dow Chemical Co.	EAA, 15% AA	SAP-2	09	40	250-260	Yes
	AN	PRIMACOR blend (b)	Dow Chemical Co.	EAA, 15% AA	SAP-2	20	20	250-260	8
9-	-	PRIMACOR 3460	Dow Chemical Co.	EAA, 6.5% AA	SAP-3	09	40	250-260	Yes
17		ELVALOY EP4924	DuPont	EVACO	SAP-4	09	9	250-260	Yes

a) Aqua Calk is a thermoplastic, non-ionic, water-absorbent polymer, manufactured by cross-linking polyethylene oxide
(b) 50:50 blend of PRIMACOR 3460 and PRIMACOR 5980
SAP = superabsorbent polymer
SAP-1 is a polyacrylate based superabsorbent polymer available as CABLOC 1181 from Stockhausen having a particle size distribution from about 1 to about 50 micrometers
SAP-2 is a polyacrylate based superabsorbent polymer available as CABLOC 80HS from Stockhausen having a particle size distribution from about 1 to about 500 micrometers
SAP-3 is a polyacrylate based superabsorbent polymer available as DRYTECH 2035 from Dow Chemical Company having a particle size distribution from about 1 to about 500 micrometers
SAP-4 is a polyacrylate based superabsorbent polymer available as CABLOC 88HS from Stockhausen having a particle size distribution from about 150

Comparative Examples AO to AW are different neat thermoplastic resins,

Comparative Example AU is neat superabsorbent polymer CABLOC 850-13, AV is the neat
superabsorbent polymer CABLOC 80HS, AW is the neat superabsorbent polymer CABLOC
88HS and Examples 18 to 30 are different thermoplastic resins compounded with a
superabsorbent polymer. A ZSK 58 millimeter (mm) co-rotating bi-lobe twin screw
extruder having a low shear mixing screw and 10 temperature zones is used. The
superabsorbent polymer is fed using a side port powder screw feeder between zones 4 and 5.

Mixing occurs in zone 6. The transition point between zone 8 and 9 is the vent port. There
is a kneading mixing section prior to the vent port. The temperature range for the first 3
zones is from 65 to 120°F, for zones 4 and 5 it is from 240 to 255°F, for zones 6 to 8 it is
from 320 to 335°F and for zones 9 and 10 it is from 270 to 330°F. The melt temperature is
maintained at 310°F.

The blend compositions are extruded through a 24 hole underwater die having hole diameters of 0.110 inch into a liquid bath containing a NaHCO₃ solution having a specific gravity of greater than 1.05 as measured with a desitometer with a temperature maintained below 20°C. A Gala underwater pelletizer with 3 cutting blades is used to pelletize the extrudate. The distance from the underwater pelletizer to the separating dryer is optimized to minimize the adsorption of water. Further, cool air is blown on the pellets in the pellet-collecting vessel driving away any remaining moisture on the pellets.

The absorption capacity in pure water (WAC) of the neat thermoplastic resins Comparative Examples AO to AT, the neat superabsorbent polymers Comparative Examples AU to AW and the thermoplastic superabsorbent polymer blend compositions Examples 18 to 30 is measured according to the following procedure: For the thermoplastic superabsorbent polymer blend compositions a sample determined to contain 1 gram of the superabsorbent polymer (based on the percent superabsorbent polymer in the blend composition) weighing W_1 is placed in 1.5 liter of distilled water and is shaken on a shaker for 2 hours. The water is filtered from the swollen particles through a 75 micrometer sieve. The weight of the swollen particles (W_2) is then measured. The amount of water absorbed, W_3 , is $W_2 - W_1$. For the neat resins and neat superabsorbent polymers a sample weighing 1 gram is subjected to the same procedure described herein above.

The compositions and water absorbed for Comparative Examples AO to AW and Examples 18 to 30 are shown in Table 3, the superabsorbent polymer is present in parts by weight based on the weight of the thermoplastic superabsorbent polymer blend composition

and water absorption is reported as grams of distilled water absorbed per gram of superabsorbent polymer.

Table 3

5

15

Example	Com. Ex.	Thermoplastic Resin	CABLOC 850-13, parts	CABLOC 80HS, parts	CABLOC 88HS, parts	Water Absorption, g
	AO	SURLYN 1702				. 0
18		SURLYN 1702	35			3
19		SURLYN 1702	45			212
20		PRIMACOR blend (a)	40			214
21		ELVALOY EP4924	40			231
22		PRIMACOR 3460	40			239
23		SURLYN 1702		20		2
24	-	PRIMACOR blend (a)		20		1
25		PRIMACOR blend (a)		30		2
•	AP	PRIMACOR blend (a)				0
26		PRIMACOR blend (b)		40		126
_	AQ	ELVALOY EP4924				0
27		ELVALOY EP4924		20		2
28	-	PRIMACOR 3460		40]	118
	AR	XUS60751.17				0
29		SURLYN 1702			35	1
	AS	PRIMACOR 1430		<u> </u>		0
30		SURLYN 1702			45	96
	AT	PRIMACOR 5980		 -		0
	AU		100			172
	AV			100		198
	AW				100	153

(a) 50:50 blend of PRIMACOR 3460 / PRIMACOR 5980

10 Thermoplastic Superabsorbent Polymer Blended with Polyethylene

In Examples 31 to 38 thermoplastic superabsorbent polymer is melt blended in a Brabender Plasticoder with a 70:30 LLDPE:LDPE polymer blend. The thermoplastic superabsorbent polymer comprises 40 weight percent CABLOC T5066-F which is a sodium polyacrylate superabsorbent polymer that is surface cross-linked having a particle size distribution of about 1 to about 60 micrometers available as a powder from Stockhausen and supplied by the Stewart Superabsorbents LLC and 60 weight percent of a 50:50 PRIMACOR 5980:PRIMACOR 3460 polymer blend. The Brabender Plasticoder conditions are: Barrel temperature is set at 275°F; Mixing RPM is 80; and Mixing times range from 1.5 to 2 minutes. A melt indexer is used to determine the melt flow rate, melt

⁽b) 50:50 blend of PRIMACOR 1430 and XUS 60751.17 (EAA with 20.5% PAA)

tension and melt draw down rate of the polymer blends. The blend compositions are considered extrudable. The compositions of Examples 31 to 38 and their MFR, melt tension and draw rates are given in Table 4.

Table 4

ехатріе	Thermoplastic Resin:Superabsorbent Polymer " A " .	LLDPE:LDPE Blend Ratio polymer blend A:B "B"	Blend Ratio A:B	MFR, Condition	MFR, g/10 min Melt Tension, units	Melt Tension, units	Draw Rate, fpm	Extrudable
31	60:40 PRIMACOR BLEND:CABLOC T5066F	70:30 LLDPE:LDPE	90:10	၁	3.51	2.0	20	Yes
83	60:40 PRIMACOR BLEND:CABLOC T5066F	70:30 LLDPE:LDPE	80:20	O	4.43	0.8	48	Yes
æ	60:40 PRIMACOR BLEND:CABLOC T5066F	70:30 LLDPE:LDPE	60:40	O	6.01	6.0	48	Yes
\$	60:40 PRIMACOR BLEND:CABLOC T5066F	70:30 LLDPE:LDPE	20:80	O	6.17	1.0	34	Yes
35	60:40 PHIMACOR BLEND:CABLOC T5086F	70:30 LLDPE:LDPE	90:10	ш	24.7	0.5	100	Yes
36	60:40 PRIMACOR BLEND:CABLOC T5066F	70:30 LLDPE:LDPE	80:20	ш	25.7	9.0	100	Yes
37	60:40 PRIMACOR BLEND:CABLOC T5066F	70:30 LLDPE:LDPE	60:40	ш	28.1	0.7	100	Yes
æ	60:40 PRIMACOR BLEND:CABLOC T5066F	70:30 LLDPE:LDPE	20:80	ш	21.9	0.8	100	Yes
88	38 60:40 70:30 PRIMACOR BLEND:CABLOC T5066F LLDPE:L		70:30 LDPE:LDPE	DPE	20:80 DPE	DPE 20:80 E	DPE 20:80 E 21.9	DPE 20:80 E 21.9 0.8

PRIMACOR BLEND: 50:50 blend of PRIMACOR 3460/PRIMACOR 5980

LLDPE = linear low density polyethylene

LDPE = low density polyethylene

Condition E = 190°C/2.16 kg

Condition C = 150°C/2.16 kg

Monolayer Films

5

10

15

20

25

Examples 39 to 42 are monolayer films of thermoplastic superabsorbent polymer blend compositions produced using a cast line process. The thermoplastic superabsorbent polymer blend compositions comprise a thermoplastic resin and CABLOC 850-13. The temperature zones for the cast film process range from 250°F to 320°F. The feedblock and die temperatures range from 270°F to 320°F. Smooth to textured uniformed film having a thickness greater than 6.0 mils or web film having a thickness less than 6.0 mils can be made depending on the take up speed.

The compositions and properties of monolayer films Examples 39 to 42 are shown in Table 5, the superabsorbent polymer is present in parts by weight based on the weight of the thermoplastic superabsorbent polymer blend composition. Absorption capacity in pure water was determined by as described hereinabove.

Table 5

Example	Thermoplastic Resin	CABLOC	Water Absorption, g
		850-13, parts	
39	SURLYN 1702	35	25
40	SURLYN 1702	45	226
41	PRIMACOR blend (a)	40 .	219
42	ELVALOY EP4924	40	238

(a) 50:50 blend of PRIMACOR 3460 / PRIMACOR 5980

Monolayer Films Containing Surfactant

Examples 43 to 46 are mono layer films containing a surfactant. The thermoplastic superabsorbent polymer is melt blended in a Brabender Plasticoder with a commercially available polyethylene containing surfactant compound. The polyethylene containing surfactant is available from AMPACET as ANTIFOG PE MB and contains 10 weight percent active surfactant, mono- and di- glycerides, in a LLDPE/LDPE base polymer. The thermoplastic superabsorbent polymer comprises 40 weight percent CABLOC T5066-F a sodium polyacrylate superabsorbent polymer that is surface cross-linked having a particle size distribution of about 1 to about 60 micrometers available as a powder from Stockhausen and supplied by the Stewart Superabsorbents LLC and 60 weight percent of a 50:50 PRIMACOR 5980:PRIMACOR 3460 polymer blend. The Brabender Plasticoder conditions are: Barrel temperature is set at 275°F; Mixing RPM is 80; and Mixing times

range from 1.5 to 2 minutes. Water absorption and rate of absorption is measured by placing a 2 inch disc sample of a 5 to 7 mil compression molded film in a 2 inch diameter cylinder. At the bottom of the cylinder is a fine mesh screen that is 75 micronmeter or less. A Teflon disk is placed on top of the film sample to secure it in place during the testing. The cylinder containing the sample is placed on top of 4 inch glass fret so that the film sample and screen faced the glass fret. A filter paper is placed between the cylinder and the glass fret. The glass fret, filter and the cylinder is placed in a container that contains water so that the height of the water reaches the height of the glass fret. The water continuously being removed and replenished. The entire set up sits on a Mettler PG3001-S balance. Once the cylinder containing the sample is placed on the balance, the balance is tared and water absorption and water absorption rate data is generated using a Mettler BalanceLink data acquisition software package. Table 6 lists the compositions for Examples 43 to 46 and their water adsorption amounts and rates.

Table 6

Example	Thermoplastic	AMPACET	Water	Time to reach	Time to reach
ļ	superabsorbent	polymer,	Absorption, g	50% of	maximum
	polymer, parts	parts		absorption value,	absorption value,
				sec	sec
43	100	0	1	55	225
44	90	10	2.2	40	80
45	80	20	2.6	60	120
46	20	80	1.4	45	80

Thermoplastic superabsorbent polymer = 60 weight percent 50:50 PRIMACOR 5980;PRIMACOR 3460 polymer blend + 40 weight percent CABLOC T5066-F

20 Multilayer Films

25

5

10

Comparative Examples AX to AZ and Examples 47 to 49 are multilayer films of thermoplastic superabsorbent polymer blend compositions produced using a blown film process. The extruder temperature zones for the thermoplastic superabsorbent polymer blend composition (layer 1) range from 250°F to 300°F. Depending on the polymer used, the extruder temperature zones for layers 2 and 3 range from 250°F to 400°F and die temperatures range from 250°F to 400°F. The compositions and descriptions of multilayer blown film Comparative Examples AX to AZ and Examples 47 to 49 are shown in Table 7.

Examples 50 to 53 are multilayer blown films prepared as described herein above wherein the level of CABLOC 850-13 is varied in a PRIMACOR blend resin while the composition and ratios of layers 2 and 3 are kept constant. The absorption capacity as described hereinabove and the time to gel block in pure water is determined. The time for the superabsorbent polymer to gel the water at its absorption capacity in pure water for the superabsorbent films, referred to as gel block, is measured according to the following procedure. A sample of the thermoplastic superabsorbent film composition comprising 0.15 gram of superabsorbent polymer in a vial containing 25.6 grams of distilled water. The mixture was shaken by hand until it was gel blocked. The swell initiation time is the time from when the water is added to the first observable swelling of the superabsorbent polymer.

5

10

15

Table 8 lists the compositions and film gauge for multilayer films Comparative Example AAA and Examples 50 to 53. Table 9 lists the water absorption, swell initiation time and time to gel block properties for multilayer films Comparative Examples AAA and Examples 50 to 53 and neat CABLOC 850-13 (Comparative Example AAB).

Table 7

		r.		e.		ē		္င	,	و		ဥ	
Product description		Frequent pinholes in film,	die face build-up	Frequent pinholes in film,	die face build-up	Some pinholes in film, die	face build-up	Ran well, no pinholes, no	die face build-up.	Ran well, no pinholes, no	die face build-up.	Ran well, no pinholes, no	die face build-up.
Gauge	aim	4.0		5.0		4.5		1.0-2.3		2.3		2.3	
0	က	20		50		50		50		50		82	
Layer ratio	2	09		8		8		22		20		20	
	-	82	•	ଷ		ଷ		ຂ		ဧ		ၕ	
Layer 3 composition		100% PRIMACOR 3330		100% PRIMACOR 3330		100% PRIMACOR 3330		100% PRIMACOR 3330		100% PRIMACOR 3330		100% PRIMACOR 3330	
Layer 2 composition Layer 3 composition		100% ATTANE 4201		20% ATTANE 4201	80 % LDPE 681	100% ATTANE 4201		30% ATTANE 4201	70% LDPE 681	50% ENGAGE 8100	50% LDPE 681	80% ATTANE 4402	20% LDPE 681
Example Com. Ex. Layer 1 composition		20 parts CABLOC 1181	80 parts LDPE 681	30 parts CABLOC 1181	70 parts ELVAX 3180	30 parts CABLOC 80HS	70 parts PRIMACOR 3330	40 parts CABLOC 80HS	60 parts PRIMACOR 3460	40 parts CABLOC 88HS	60 parts ELVALOY 4924	40 parts CABLOC 850-13	60 parts PRIMACOR blend (a)
Com. EX.		¥		ΑY		ΑZ							
Examble								47		48		46	

(a) 50:50 blend of PRIMACOR 3460 / PRIMACOR 5980

Table 8

	<u> </u>	_		_		<u> </u>		Γ			
Gauge	sim	4.0		2.0		4.5		1.0-2.3		2.3	
	3	ୟ		50		ಽ		20		ಜ	
Layer ratio	2	20		20		20		20		20	
	-	30		30		೫		8		30	
Layer 3 composition		100% PRIMACOR 3330		100% PRIMACOR 3330		100% PRIMACOR 3330		100% PRIMACOR 3330		100% PRIMACOR 3330	
Layer 2 composition		80% ATTANE 4201	20% LDPE 681	80% ATTANE 4201	20% LDPE 681	80% ATTANE 4201	20% LDPE 681	80% ATTANE 4201	20% LDPE 681	80% ATTANE 4201	20% LDPE 681
Example Com. Ex. Layer 1 composition		100% PRIMACOR blend (a)		10 parts CABLOC 850-13	90 parts PRIMACOR blend (a) 20% LDPE 681	20 parts CABLOC 850-13	80 parts PRIMACOR blend (a) 20% LDPE 681	30 parts CABLOC 850-13	70 parts PRIMACOR blend (a) 20% LDPE 681	40 parts CABLOC 850-13	60 parts PRIMACOR blend (a) 20% LDPE 681
Com. Ex.		AAA									
Example				20		51		52		53	

(a) 50:50 blend of PRIMACOR 3460 / PRIMACOR 5980

Table 9

Time to Gel Block, sec		Did not gel block	840-900	360-420	90-200	06-09
Swell Initiation Time, sec		< 15	<15	<10	\$	\$>
Water Absorption, g	0	127.25	203.3	225.9	257.65	180.0
Com. Ex.	AAA					AAB
Example		20	51	25	23	

Multilayer Films Coated with a Surfactant Solution

5

10

15

25

Examples 54 to 57 use a 2.0 mil multilayer blown film. The multilayer film comprises as layer 1 a thermoplastic superabsorbent polymer blend comprising 60 weight percent of a 50:50 blend of PRIMACOR 3460 / PRIMACOR 5980 and 40 weight percent CABLOC T5066 F, as layer 2 a LDPE 4005 and as layer 3 PLEXAR 107 an EVA g-MAH from Equistar. The extruder temperature zones for the thermoplastic superabsorbent polymer blend composition (layer 1) range from 250°F to 300°F, the zone temperatures for layer 2 range from 305°F to 310°F and the zone temperatures for layer 3 range from 350°F to 370°F. The thickness ratio for layers 1:2:3 is 30:50:20. Layer 1, the thermoplastic superabsorbent layer, of the multilayer film is sprayed with a surfactant solution ranging from 0 to 8 percent surfactant. The surfactant used for the study is an alcohol ether sulfate. After the film is sprayed, it is placed in an air circulating oven to dry at a temperature of 50°C for 1-2 minutes. Water absorption and rate of absorption is measured according to procedures in the aforementioned section. Table 10 summarizes the water absorption amounts and rates for Examples 54 to 57.

Table 10

Example	Surfactant	Water	Time to initial	Time to reach	Time to reach
	solution, %	Absorption,	absorption,	50% of	maximum
		g	sec	absorption value,	absorption value,
				sec	sec
54	0	1.7	15	60	170
55	2	2.0	0	31	112
56	5	1.9	0	29	160
57	8	1.8	0	27	135

20 Superabsorbent Film and Metal Laminate

Example 58 is the multilayer film described in Example 53 laminated to 6.0 mils Electrically Chrome Coated Steel (ECCS) via a heat lamination process. The adhesive layer of the film (layer 3) is used to bond the film to the steel surface. The superabsorbent film/metal laminate can find usefulness in power cable and communication cable construction. The metallic substrate can provide shielding and the thermoplastic superabsorbent polymer layer can be used to bond to itself or another substrate and can

function to stop, block and absorb water in cables. Table 11 shows the adhesion properties for Example 57 superabsorbent film and metal laminate.

Table 11

5

10

15

20

25

30

Example	Film	Metal Type	Peel Strength (a),	Heat Seal (a)	Jacket (b) Bond
			(lb/in)	Strength, (lb/in)	Strength, (lb/in)
58	Example 53	ECCS	5.0	13.1	31.8

⁽a) Peel strength and heat seal strength are measured according to ASTM B 736 and heat seal strength is the bond strength of the thermoplastic superabsorbent polymer to itself.

ECCS = electrically chrome coated steel

Armored Cable

Superabsorbent films were laminated to the ECCS and slit into 2.25 inch wide steel tape. The tape is used to make armored cables Examples 59 to 62. The steel tape is corrugated to 32 corrugations per inch (corrugation can be achieved with or without oil). The corrugated tape is longitudinal formed through a series of forming dies. A PVC jacketed insulated copper pair cable core having an outside diameter of 0.60 inch is placed inside the formed armored tape. A jacketing resin is then extruded onto the formed armored tape to make a final cable having a final outside diameter of 0.742 inch. The final gap between the inner jacket and the armor tape is calculated to be around 0.015 inch (0.381mm).

The performance of cables comprising the thermoplastic superabsorbent polymer laminate (Examples 59 to 62, Table 12) is compared to cables comprising ZETABON CJBS262 armor tape available from the Dow Chemical Company (Comparative Example AAC) and additionally comprising a non-woven superabsorbent tape 3E252 produced by Lantor Inc. (Comparative Example AAD). Non-woven superabsorbent tapes are the wire and cable industry standard for use in dry cable designs. The non-woven superabsorbent tape comprises superabsorbent particles sandwiched between two non-woven materials. For this evaluation, the non-woven superabsorbent tape is helically wrapped around the copper pair cable core before placing the cable core inside the formed armor tape. In the wire and cable industry, the non-woven superabsorbent tape is typically longitudinal formed around the cable core.

⁽b) Jacketing material is DFDD 6069 BK 9865 a modified LLDPE which is a standard wire and cable jacketing resin manufactured by Union Carbide. Jacket bond (composite of Jacketing material and laminate fabricated in a platen press) strength measures the force to separate the jacket from the laminate, values is measured according to ASTM D 4365-86 modified to hold the sample at 180°C.

Water blocking performance of the cables is determined by the EIA/TIA-455-82A ("L-test"). The end of the cable core is taped or sealed so that water can not migrate through the wires of the cable core. The cable length is 1 meter, test duration is 24 hours, the water column is 1 meter and time to penetration is measured.

5

15

20

Table 12

Example	Com. Ex.	Laminate composition			Non-woven tape	Time to penetration
		Film Layer 1	Metallic Core	Film Layer 2		
	AAC	EAA film	6 mil ECCS	EAA film	No	Within 1 minute
	AAD	EAA film	6 mil ECCS	EAA film	Yes	(a)
59		EAA film	6 mil ECCS	Film 1	No	No penetration
60		EAA film	6 mil ECCS	Film 2	No	No penetration
61		EAA film	6 mil ECCS	Film 3	No	No penetration
62		EAA film	6 mil ECCS	Film 4	No	No penetration

(a) test results vary from no penetration to penetration occurring between 15-24 hours

EAA film = 90% PRIMACOR 3330 / 10% PE

10 Film 1 composition:

Layer 1: 30% - 40 parts CABLOC 850-13 / 60 parts (50/50 PRIMACOR 3460/PRIMACOR 5980)

Layer 2: 50% - 80% ATTANE 4201 / 20% LDPE 681

Layer 3: 20% - PRIMACOR 3330

Film 2 composition:

Layer 1: 30% - 40 parts CABLOC 80HS / 60 parts (50/50 PRIMACOR 3460/PRIMACOR 5980)

Layer 2: 50% - 80% ATTANE 4201 / 20% LDPE 681

Layer 3: 20% - PRIMACOR 3330

Film 3 composition:

Layer 1: 30% - 40 parts CABLOC 1181 / 60 parts (50/50 PRIMACOR 3460/PRIMACOR 5980)

Layer 2: 50% - 80% ATTANE 4201 / 20% LDPE 681

Layer 3 20% - PRIMACOR 3330

Film 4 composition:

Layer 1 30% - 40 parts CABLOC 80HSB / 60% (50/50 PRIMACOR 3460/PRIMACOR 5980)

Layer 2 50% - 80% ATTANE 4201 / 20% LDPE 681

Layer 3 20% - PRIMACOR 3330

CABLOC 80HSB has a particle size distribution from about 1 to about 20 micrometers

Film Layer 1 is the side of the laminate that is used to bond to the jacketing resin

Film Layer 2 is the side of the laminate that was facing the core

Armor Cable with Thermoplastic Superabsorbent Polymer Coated with a Surfactant

Superabsorbent films were laminated to the ECCS. The superabsorbent layer of the film is either pre- or post-coated with an alcohol ether sulfate surfactant solution. The concentration of the surfactant solution ranges from 2 weight percent to 8 weight percent.

An antifoaming agent, Dow Corning Anti Foam 1520-US, is also used. The amount of antifoam used is 2500 ppm. The coated laminate is slit into 1.375 inch wide steel tape. The tape is used to make armored cables Examples 63 to 68 (Table 13). The steel tape is corrugated to 32 corrugations per inch (corrugation can be achieved with or without oil). The corrugated tape is longitudinal formed through a series of forming dies. An HDPE core tube, available from United States Plastic Corporation, having an outside diameter of 0.375

inch is placed inside the formed armored tape. A jacketing resin is then extruded onto the formed armor tape to make a final cable. The final gap between the inner jacket and the armor tape is calculated to be around 0.020 inch (0.508mm).

The performance of cables comprising the thermoplastic superabsorbent polymer laminate (Examples 63 to 68) is compared to cables comprising ZETABON C.IBS262 armor tape available from the Dow Chemical Company (Comparative Example AAC).

Water blocking performance of the cables is determined by the EIA/TIA-455-82A ("L-test"). The end of the cable core is taped or sealed so that water can not migrate through the wires of the cable core. The cable length is 1 meter, test duration is 24 hours, the water column is 1 meter and time to penetration is measured.

Table 13

Example	Com. Ex.	Laminate composition			Surfactant treatment	Time to penetration
		Film Layer 1	Metallic Core	Film Layer 2		
	AAC	EAA film	6 mil ECCS	EAA film		Within 1 minute
63		EAA film	6 mil ECCS	Film 1	Pre-	Pass
64		EAA film	6 mil ECCS	Film 2	Pre-	Pass
65		EAA film	6 mil ECCS	Film 2	Post-	Pass
66		EAA film	6 mil ECCS	Film 2	Post-	Pass
67		EAA film	6 mil ECCS	Film 3	Post-	Pass
68		EAA film	6 mil ECCS	Film 3	Post-	Pass

EAA film = 90% PRIMACOR 3330 / 10% PE

10

15

20

25

Film 1 composition: Layer 1: 30% - 40 parts CABLOC 850-13 / 60 parts (50/50 PRIMACOR 3460/PRIMACOR 5980)

Layer 2: 50% - LDPE 4005 Layer 3: 20% - PIEXAR 107

Film 2 composition: Layer 1: 30% - 40 parts CABLOC T5066 F / 60 parts (50/50 PRIMACOR 3460/PRIMACOR 5980)

Layer 2: 50% - LDPE 4005

30 Layer 3: 20% - PIEXAR 107

Film 3 composition: Layer 1: 30% - 40 parts Norscoryl XFS / 60 parts (50/50 PRIMACOR 3460/PRIMACOR 5980)

Layer 2: 50% - LDPE 4005 Layer 3 20% - PIEXAR 107

Norsocryl is a crosslinked copolymers of acrylic acid and sodium acrylate supplied by elf atochem ATO

PLEXAR 107 is a grafted maleic anhydride EVA copolymer supplied by Equistar

Film Layer 1 is the side of the laminate that is used to bond to the jacketing resin

Film Layer 2 is the side of the laminate that was facing the core

Foam Thermoplastic Superabsorbent Polymer

5

10

15

25

30

Examples 69 to 77 are extruded foams of thermoplastic superabsorbent polymer blend compositions. About 12 parts per hundred (pph) HCFC 142B physical blowing agent is used. The extruder temperature zones range from 110°C to 150°C and the die temperature range from 85°C to 90°C. The compositions and description of the foam are shown in Table 14. The resulting foams are soft, flexible and non-friable. The superabsorbent particulates are uniformly distributed on the skin and throughout the cell structure of the foam.

Table 14

Example	Thermoplastic superabsorbent polymer type	Foam type
69	1	Semi-porous to closed cell foam
70	2	Semi-porous to closed cell foam
71	3	Semi-porous to closed cell foam
72	4	Semi-porous to closed cell foam
73	5	Semi-porous to closed cell foam
74	. 6	Semi-porous to closed cell foam
75	7	Semi-porous to closed cell foam
76	8	Semi-porous to closed cell foam
77	9	Semi-porous to closed cell foam

20 1 composition: 10 parts CABLOC T5066 F / 60 parts (50/50 PRIMACOR 3460/PRIMACOR 5980)

2 composition: 20 parts CABLOC T5066 F / 60 parts (50/50 PRIMACOR 3460/PRIMACOR 5980)

Norsocryl is a crosslinked copolymers of acrylic acid and sodium acrylate supplied by elf atochem ATO

Norsocryl XFS particle size distribution range from 1-67 micronmeter

Norsocryl S25 particle size distribution range form 1-225 micronmeter

³ composition: 30 parts CABLOC T5066 F / 60 parts (50/50 PRIMACOR 3460/PRIMACOR 5980)

⁴ composition:30 parts CABLOC 80 HS / 60 parts (50/50 PRIMACOR 3460/PRIMACOR 5980)

⁵ composition:20 parts CABLOC HCF / 60 parts (50/50 PRIMACOR 3460/PRIMACOR 5980)

⁶ composition: 20 parts Norsocryl XFS / 60 parts (50/50 PRIMACOR 3460/PRIMACOR 5980)

⁷ composition: 20 parts Norsocryl S35 / 60 parts (50/50 PRIMACOR 3460/PRIMACOR 5980)

⁸ composition:30 parts Norsocryl S35 / 60 parts (50/50 PRIMACOR 3460/PRIMACOR 5980)

⁹ composition: 35 parts Norsocryl S35/ 60 parts (50/50 PRIMACOR 3460/PRIMACOR 5980)

The absorption capacity in pure water (WAC) of thermoplastic superabsorbent foam Examples 78 to 80 (Table 15) extruded by the abovementioned extrusion foam process is shown in Table 16. The WAC is measured according to the following procedure: the foam is cut in 0.125 inch by 0.625 in by 0.1.25 to 0.25 inch and an amount of the cut foam sample determined to contained 0.1 gram of the superabsorbent polymer (based on the percent superabsorbent polymer in the foam composition) weighing W1 is placed in 0.150 liter of distilled water and is shaken on a shaker for 2 hours. The water is filtered from the foam through a 75 micrometer sieve. The weight of the swollen foam (W2) is then measured. The amount of water absorbed, (Wa) is calculate by the following formula:

10

5

Wa = (W2-W1) * 10

Table 15

Example	Thermoplastic superabsorbent polymer type	Foam	Water absorption, g
78	2	Yes	87
79	3	Yes	67
80	3	Yes	43

15

20

2 composition: 3 composition:

20 parts CABLOC T5066 F / 60 parts (50/50 PRIMACOR 3460/PRIMACOR 5980) 30 parts CABLOC T5066 F / 60 parts (50/50 PRIMACOR 3460/PRIMACOR 5980)

9 composition:

35 parts Norsocryl \$35/60 parts (50/50 PRIMACOR 3460/PRIMACOR 5980)

From these data it can be concluded that the extrudable thermoplastic superabsorbent polymer blends of the present invention comprising one or more superabsorbent polymer and one or more thermoplastic resin wherein the thermoplastic resin comprises a functional group that interacts with the superabsorbent polymer yields the best balance of superabsorbent polymer containment, processability, formability and absorption properties.

25

It has been found that the present invention provides improved thermoplastic superabsorbent polymer blend compositions and processes for preparing, among other things, monolayer films, multilayer films, nonwoven webs, sheets, foams, profiles, multilayer laminates, fibers, tubes, rods, and pipes. It can be seen that the resulting parts or structures according to the present invention are surprisingly improved by the use of the

described extrudable thermoplastic superabsorbent polymer blend compositions and that extruded, shaped or otherwise fabricated articles will ease manufacture, improve performance and reduce costs of absorbent articles constructed therefrom.

CLAIMS:

5

10

15

20

25

30

1. An extrudable thermoplastic superabsorbent polymer blend composition comprising

- (a) one or more superabsorbent polymer and
- (b) one or more thermoplastic resin comprising a functional group which interacts ionically or covalently with (a).
- 2. The extrudable thermoplastic superabsorbent polymer blend composition of Claim 1 having a melt draw down rate between about 5 and about 100 feet per minute and a melt tension between about 0.1 and about 10 under temperature and applied load conditions that give a melt flow rate of between about 0.1 and about 300 g/10 min.
- 3. The extrudable thermoplastic superabsorbent polymer blend composition of Claim 1 wherein the superabsorbent polymer is prepared from water-soluble α,β -ethylenically unsaturated monomers.
- 4. The extrudable thermoplastic superabsorbent polymer of Claim 3 wherein the α,β -ethylenically unsaturated monomers is a monocarboxylic acid, a vinyl polycarboxylic acid, an acrylamide or mixtures thereof.
- 5. The extrudable thermoplastic superabsorbent polymer blend composition of Claim 1 wherein the superabsorbent polymer is a cellulosic-graft copolymer, a starch-graft copolymer, a starch-g-poly(acrylic acid), a polyacrylamide; a polyvinyl alcohol, a poly(acrylic acid), a copolymer of sulfonic acid group containing monomer, or mixtures thereof.
- 6. The superabsorbent polymer of Claim 5 is crosslinked, partially neutralized, surface treated or combinations thereof.
- 7. The extrudable thermoplastic superabsorbent polymer blend composition of Claim 1 wherein the thermoplastic resin is a polyacrylic acid, ethylene and acrylic acid copolymer, ethylene, t-butylacrylate and acrylic acid terpolymer, ethylene and methacrylic acid copolymer, ionomers of ethylene and methacrylic acid copolymers, ethylene, vinyl acetate and carbon monoxide terpolymer, ethylene and carbon monoxide copolymer, ethylene, acrylic acid and carbon monoxide terpolymers, ethylene, n-butylacrylate and carbon monoxide terpolymer or blends thereof.
- 8. The extrudable thermoplastic superabsorbent polymer blend composition of Claim 1 further comprising a surfactant.

9. The extrudable thermoplastic superabsorbent polymer blend composition of Claims 1, 3 or 8 further comprising a polyethylene, a copolymer of polyethylene, a polypropylene, a copolymer of polypropylene or a polystyrene.

- 10. A method for preparing an extrudable thermoplastic superabsorbent polymer blend composition comprising the step of combining:
 - (a) one or more superabsorbent polymer and

5

15

25

30

- (b) one or more thermoplastic resin comprising a functional group which interacts ionically or covalently with (a).
- 11. The method of Claim 10 further comprising the step of combining (c) a surfactant.
 - 12. A method for producing an extruded or molded article of an extrudable thermoplastic superabsorbent polymer blend composition comprising the steps of:
 - preparing an extrudable thermoplastic superabsorbent polymer composition comprising
 - (c) one or more superabsorbent polymer and
 - (b) one or more thermoplastic resin comprising a functional group which interacts ionically or covalently with (a) and
 - 2) extruding or molding said thermoplastic superabsorbent polymer composition into an extruded or molded article.
- 13. The method of Claim 12 wherein the superabsorbent polymer composition further comprising (c) a surfactant.
 - 14. The method of Claims 12 or 13 wherein the extruded article is a monolayer film, a multilayer film, a nonwoven web, a sheet, a foam, a profile, a multilayer laminate, a fiber, a tube, a rod or a pipe.
 - 15. The method of Claims 12 or 13 wherein the extruded article is a monofilament fiber, a bicomponent monofilament fiber, a spun bond nonwoven web, a melt blown nonwoven web, or a composite comprising combinations thereof.
 - 16. The method of Claims 12 or 13 wherein the extruded article is a nonwoven web comprising a spun bond nonwoven web comprising one or more bicomponent fiber, a melt blown nonwoven web comprising one or more bicomponent fiber, or a composite structure comprising at least one layer of one or more spun bond nonwoven web and at least one layer of one or more melt blown nonwoven web wherein one or more layers of the composite comprise bicomponent fibers.

17. The composition of Claims 1 or 8 in the form of an extruded or molded article.

- 18. The extruded or molded article of Claim 17 is a monolayer film, a multilayer film, a nonwoven web, a sheet, a foam, a profile, a multilayer laminate, a fiber, a tube, a rod or a pipe.
- 19. The extruded or molded article of Claim 17 is a monofilament fiber, a bicomponent monofilament fiber, a spun bond nonwoven web, melt blown nonwoven web, or a composite comprising combinations thereof.

5

10

15

20

- 20. The extruded or molded article of Claim 17 is a nonwoven web comprising a spun bond nonwoven web comprising one or more bicomponent fiber, a melt blown nonwoven web comprising one or more bicomponent fiber, or a composite structure comprising at least one layer of one or more spun bond nonwoven web and at least one layer of one or more melt blown nonwoven web wherein one or more layers of the composite comprise bicomponent fibers.
 - 21. The monolayer film or multilayer film of Claim 18 laminated to a metal.
 - 22. A power cable comprising the metal laminate of Claim 21.
 - 23. A communications cable comprising the metal laminate of Claim 21.
 - 24. A power cable comprising the monolayer film or multilayer film of Claim 18.
- 25. A communications cable comprising the monolayer film or multilayer film of Claim 18.
- 26. A disposable absorbent device comprising an extruded or molded article of Claim 18.
- 27. The disposable absorbent device of Claim 26 is a diaper, a sanitary napkin, a tampon, an incontinence product, a hospital gown or a bed pad.
- 28. A disposable absorbent device comprising an extruded or molded article ofClaim 19.
 - 29. The disposable absorbent device of Claim 28 is a diaper, a sanitary napkin, a tampon, an incontinence product, a hospital gown or a bed pad.
 - 30. A disposable absorbent device comprising an extruded or molded article of Claim 20.
- 31. The disposable absorbent device of Claim 30 is a diaper, a sanitary napkin, a tampon, an incontinence product, a hospital gown or a bed pad.

(19) World Intellectual Property Organization International Bureau



(43) International Publication Date 31 January 2002 (31.01.2002)

PCT

(10) International Publication Number WO 02/07791 A3

- (51) International Patent Classification⁷: C08L 101/14, A61L 15/60, 15/22, B32B 27/30
- (21) International Application Number: PCT/US01/21869
- (22) International Filing Date: 11 July 2001 (11.07.2001)
- (25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data: 60/220,529

24 July 2000 (24.07.2000) US

- (71) Applicant: DOW GLOBAL TECHNOLOGIES INC. [US/US]; Washington Street, 1790 Building, Midland, MI 48674 (US).
- (72) Inventor: ACHILLE, Felix; 2861 North Tupelo Drive, Midland, MI 48642 (US).
- (74) Agent: CHRISTY, M., Robert; The Dow Chemical Company, Intellectual Property, P.O. Box 1967, Midland, MI 48641-1967 (US).

- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments
- (88) Date of publication of the international search report: 25 April 2002

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



INTERNATIONAL SEARCH REPORT

Int tional Application No PCT/US 01/21869

PCT/US 01/21869 CLASSIFICATION OF SUBJECT MATTER PC 7 CO8L101/14 A61L A61L15/60 A61L15/22 B32B27/30 According to International Patent Classification (IPC) or to both national classification and IPC **B. FIELDS SEARCHED** Minimum documentation searched (classification system followed by classification symbols) CO8L CO8J A61L CO8G B32B Documentation searched other than minimum documentation to the extent that such documents are included. In the fields searched Electronic data base consulted during the International search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ, COMPENDEX C. DOCUMENTS CONSIDERED TO BE RELEVANT Category ° Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. X WO 91 18042 A (DOW CHEMICAL CO) 1,3-6,8,28 November 1991 (1991-11-28) 10,17, 18,26,27 claims 1,7,8 page 3, line 6 - line 14 X WO 99 57201 A (FULLER H B LICENSING FINANC 1,7,10, :AHMED SHARF U (US); CLAPP LESLIE J (U) 14,26 11 November 1999 (1999-11-11) claims 1,2,10,13,20,24 X WO 92 19680 A (NOVAMONT SPA) 1,5 12 November 1992 (1992-11-12) claims 1,26 Α EP 0 272 682 A (KIMBERLY CLARK CO) 1 29 June 1988 (1988-06-29) claim 1 -/--Further documents are listed in the continuation of box C. X X Patent family members are listed in annex. Special categories of cited documents: 'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the *A* document defining the general state of the art which is not considered to be of particular relevance invention *E* earlier document but published on or after the international *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such docu-'O' document referring to an oral disclosure, use, exhibition or ments, such combination being obvious to a person skilled 'P' document published prior to the international filing date but later than the priority date claimed "&" document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report 20 February 2002 06/03/2002 Name and mailing address of the ISA Authorized officer European Patent Office, P.B. 5818 Patentlaan 2

1

NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.

Fax: (+31-70) 340-3016

Hillebrand, G

IPTERNATIONAL SEARCH REPORT

Int .tional Application No PCT/US 01/21869

0.10==1:=	NATA DOCUMENTS CONSIDERED TO BE DELEVANT	101/03 01/21809				
	Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No.					
Category *	onation of document, with indication, where appropriate, of the relevant passages	neevant to claim No.				
A	EP 0 338 393 A (KIMBERLY CLARK CO) 25 October 1989 (1989-10-25) claim 1	1				

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int :ional Application No PCT/US 01/21869

				PCT/US	01/21869
Patent document cited in search report		Publication date		Patent family member(s)	Publication date
WO 9118042	А	28-11-1991	AU CA EP WO	7863091 A 2082623 A1 0530231 A1 9118042 A1	10-12-1991 20-11-1991 10-03-1993 28-11-1991
WO 9957201	A	11-11-1999	AU BR CN EP WO	3891899 A 9910261 A 1308654 T 1084194 A1 9957201 A1	23-11-1999 02-01-2001 15-08-2001 21-03-2001 11-11-1999
WO 9219680	A	12-11-1992	ETTTTTTUUUURRAANNZZZEEEEKOPSIRUPPRKVVOLUKUSSTEEKODDDDDDDDDDDDDDRVDPRSRUUADDDKLLNPRSRUUADDDK	0525245 A1 1245485 B 125693 B 1263114 B 155161 T 658180 B2 1650992 A 658207 B2 2058292 A 9203064 A 9205258 A 2074649 A1 2084994 A1 1071588 A 1077966 A ,B 9202395 A3 285748 B6 9203901 A3 9219021 U1 69220754 D1 69220754 D1 69220754 T2 539541 T1 539541 T3 9219680 A1 0539541 A1 2103943 T3 925978 A 3024078 T3 216971 B 5228205 A 2527523 B2 6502676 T 9608112 B1 12151 A 12151 B 925049 A 295469 A1 2095379 C1 390192 A3 2089151 C1 5286770 A 5412005 A 127034 T 69204351 D1 69204351 D1 69204351 T2 512360 T3	03-02-1993 20-09-1994 12-12-1995 30-07-1996 15-07-1997 06-04-1995 21-12-1992 06-04-1993 30-03-1993 27-07-1993 02-02-1993 04-11-1992 05-05-1993 17-02-1993 13-10-1999 13-10-1999 13-10-1997 14-08-1997 14-08-1997 15-09-1997 12-11-1992 05-05-1993 01-10-1997 31-12-1992 31-10-1997 31-12-1992 31-10-1997 31-12-1992 31-10-1997 28-10-1998 24-03-1994 20-06-1996 20-10-1998 20-12-1998 30-12-1998 30-12-1992 04-05-1993 10-11-1997 07-12-1994 10-09-1997 15-02-1994 10-09-1995 15-09-1995 15-09-1995
			EP	0512360 A1	11-11-1992

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int tional Application No PCT/US 01/21869

Patent document cited in search report	ļ	Publication date		Patent family member(s)	Publication date
WO 9219680	Α	· · · · · · · · · · · · · · · · · · ·	ES	2077280 T3	16-11-1995
			GR	3017583 T3	31-12-1995
			JP	3225085 B2	05-11-2001
EP 0272682	Α	29-06-1988	US	4847141 A	11-07-1989
			US	4820577 A	11-04-1989
			US	4767825 A	30-08-1988
			US	4806598 A	21-02-1989
			EP	0272682 A2	29-06-1988
			US	4963638 A	16-10-1990
			AU	658733 B2	27-04-1995
			AU	3830093 A	22-07-1993
			AU	638300 B2	24-06-1993
			AU	6805790 A	26-04-1991
			AU	632989 B2	21-01-1993
			AU	8291887 A	30-06-1988
			CA	1317694 A1	11-05-1993
			CA	1319817 A2 9700489 B1	06-07-1993
			KR KR	9700489 B1 9705111 B1	13-01-1997 12-04-1997
			US	4828911 A	09-05-1989
				4020911 A	09-05-1989
EP 0338393	Α	25-10-1989	US	4920168 A	24-04-1990
			US	4923914 A	08-05-1990
			AT	172482 T	15-11-1998
			AU	630346 B2	29-10-1992
			AU	3270489 A	19-10-1989
			CA	1339509 A1	21-10-1997
			DE	68928836 D1	26-11-1998
			DE	68928836 T2	11-03-1999
			EP	0338393 A2	25-10-1989
			ES	2123491 T3	16-01-1999
			JP JP	2043268 A	13-02-1990
			KR	3105219 B2 134626 B1	30-10-2000 20-04-1998
			KR KR	134626 B1 134667 B1	20-04-1998 20-04-1998
			US	5057262 A	20-04-1998 15-10-1991
			U.J	JUJ1 CUC 5	17.17.1331